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Fine Structure of Regenerated Cellulose Films as Revealed by Dye Accessibility*

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Synopsis

We have demonstrated the utility of dyeing techniques, using Solophenyl Fast Blue Green BL, to characterize a variety of regenerated cellulosic films. Measurement of the optical density ratio and the rate and magnitude of dye uptake show that differences in structure exist in regenerated cellulose films processed under different conditions. These differences are attributed to differences in lateral order and orientation of cellulose chains and are believed similar to the so-called skin and core observed in rayon fibers. These differences have been found related reproducibly to differences in regenerating and processing conditions. Diffusion of dye into a film is very rapid initially, slowing later to an almost constant rate, depending on the dye concentration in solution and on the type of film. A modified diffusion equation of the form $\ln C/C_0 - (1 - C/C_0) = D\gamma^2 tC_0/C_f$ has been found adequate to express the non-steady state of the observed absorption process, where C_0 is the initial dye concentration of the test solution, C is the instantaneous dye concentration at time t, C_f is the dye concentration in the film, γ^2 is the area of film per unit volume of dye solution, and D is the diffusion coefficient. Thus, a mathematical basis is provided for structural differentiation in cellulosic films processed in various ways. Plate-cast viscose films appear to have a dense surface (skin) exposed to the regenerating bath and a porous surface (core) on the side touching the plate, whereas machine-cast viscose films have a dense surface on both sides.

Study of the crystallinity and orientation of rayon fibers has greatly contributed to an understanding of the relationship between processing conditions and fiber properties, especially in the development of very strong fibers in recent years. In this report we describe a similar study of fine structure of regenerated cellulose films which was undertaken with a similar purpose: to relate and interpret the interdependence of processing variables, fine structure, and physical characteristics of the finished films.

Our approach has been to use a modification of the dye staining technique of Voss[1] and that used in the laboratories of International Cellulose Research, Ltd., Hawkesbury, Ontario. Measurements of optical density of

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films dyed with Solophenyl Fast Blue Green BL and of the rate of dye absorption have shown that differences in structure do exist in films prepared under different conditions, differences that seem interpretable in terms of molecular order.

The two regions of quite different response to dye absorption observed may be analogous to the skin and core regions that have been described in rayon fibers.[2] Variations in orientation in cellophane through the cross section of the film have been reported, but no clearly demarcated skin and core regions were found.[3]

EXPERIMENTAL

Viscose films (8 × 11 in.) were cast in the laboratory on glass plates with the aid of a casting bar set at 0.010 in. and 0.020 in. Films were regenerated at room temperature by the use of the following regenerating methods: (I) a solution of 20% sodium sulfate and 12.5% sulfuric acid; (II) sulfuric acid, 12.5%; (III) a solution of 10% zinc sulfate, 16% sodium sulfate, and 8% sulfuric acid; (IV) a 20% solution of sodium sulfate, followed by (I) (so-called two-bath system).

After 3 min. in the regenerating bath, the films were washed in flowing tap water at room temperature, cut into 3 × 4 in. pieces, and immersed in 0.2% aqueous Solophenyl Fast Blue Green BL (C.I. Direct Green 27) for 5.0 min. Excess dye solution was rinsed off, and the films were dried on a glass plate at ambient temperature. The optical density of the films was measured at 630 mμ on a Beckman Model B spectrophotometer (absorption at this wavelength is at a maximum). By use of the optical density of dyed regenerated films by method I as a standard of comparison, the ratios of optical density of all films to this standard were calculated. These ratios are listed in Table I. It is clear that the accessibility of the plate-cast films is quite different from that of the machine-cast sample. Also regeneration methods II or IV increase the accessibility greatly, whereas method III reduces it.

The machine-cast sample (which did not absorb dye) proved to have both surfaces like the plate-cast film surface in contact with the regenerating bath. The surface in contact with the glass plate could be shown to have a much greater accessibility to dye, however. Simple experiments were done in which the film was lifted from the plate after 5–15 sec. in the regen-

TABLE I
Optical Density Ratios of Regenerated Films

Film	Regeneration method	Optical density ratio
Plate-cast	I	1.00
Plate-cast	II	2.04
Plate-cast	III	0.82
Plate-cast	IV	2.40
Machine-cast	I	0.0

erating bath (method I), and then regenerated by exposing both sides to the solution. The film was folded to form a sack to hold the dye solution, and in this way either the side that had been presented to the glass plate or to the regenerating bath could be dyed separately. Thus it was found that the optical density ratio for staining the side next to the glass plate was 0.87, as compared with 0.00 for the side in contact with the regenerating solution. A sample lifted from the plate after 5 sec. and then dyed by immersion had an optical density ratio 0.44. (These are all to be compared with 1.00 by standard method I regeneration and dyeing both sides of the film.)

Rate of Dye Absorption

Having shown that the amount of dye absorbed by regenerated cellulose films provides a sensitive differentiation of the effect of various methods of regeneration, we undertook to determine the rates of dye uptake as a function of three parameters: dye concentration, film thickness, and time of dyeing.

It was found that changes in optical density could indeed be used, provided only that the sensitivity of the spectrophotometer be not exceeded, a condition that was met if less than 5 mg. of dye was taken up by a given sample of film (above this, the films were spectrophotometrically opaque). At low dye concentrations, the rate of dye pickup was much greater at the beginning than later (Table II). Also, the total amount of dye absorbed in a given time from concentrated solutions was nearly proportionate to the increase in dye concentration (Table III).

TABLE II
Optical Density of Films Dyed in 0.2% Solution

Time, min.	Optical density
2	0.30
5	0.45
7	0.60
10	0.75
20	0.87
30	1.15
60	1.75

TABLE III
Optical Density of Films Dyed for 5 Min.

Dye concentration, wt.-%	Optical density
0.02	0.12
0.05	0.18
0.10	0.26
0.20	0.45
0.50	1.35
1.00	2.25

For quantitative measurements, 3 × 6 in. film specimens were placed in 50 ml. of 0.2% aqueous dye contained in a 500-ml. wide-mouthed bottle. The rate of dye uptake by the film was then measured by determining the change of optical density of the dye solution over a time interval. At intervals, 1-ml. samples of the dye solution were diluted to 100 ml. The optical density of these solutions was measured at 630 mμ. In order to relate the optical density of the solution to the amount of dye picked up by the films, a calibration curve (optical density as a function of milligrams of dye in 100 ml.) was obtained by consecutive dilutions of a dye solution of known concentration. By use of the calibration curve, the amount of dye lost from the solution was determined and taken equal to the amount absorbed by the films.

The solution concentrations after absorption by the film could also be calculated from the extinction coefficient ϵ, with the assumption that Beer's Law is obeyed.

The optical density of each dye solution was followed as a function of time for 7 hr. Table IV presents results for measurement of optical density of films at two dye concentrations and at two film thicknesses for films prepared by two methods of regeneration. Table V compares the calculated rate of dye uptake for the two types of films (by methods I and IV) for a 7-hr. period. The calculated data were obtained from columns 2 and 4 of Table IV, by use of the calibration curve. Figure 1 compares graphically the rate of dye uptake of the two films of the same thickness regenerated by different procedures and shows conclusively that dye measurements can distinguish them.

TABLE IV
Optical Density of Dye Solutions

	Dye concn. 0.2%				Dye concn. 0.1%
	Method I		Method IV		Method I
Time, hr.	Thickness, 0.020 in.[a]	Thickness, 0.010 in.[a]	Thickness, 0.020 in.[a]	Thickness, 0.010 in.[a]	Thickness, 0.010 in.[a]
0	0.370	0.370	0.370	0.370	0.185
0.5	0.330	0.320	0.230	0.225	0.162
1.0	0.310	0.298	0.185	0.195	0.159
2.0	0.290	0.267	0.140	0.145	0.140
3.0	0.270	0.245	0.112	0.122	0.127
4.0	0.250	0.225	0.087	0.105	0.118
5.0	0.240	0.210	0.075	0.090	0.115
6.0	0.225	0.190	0.065	0.077	0.105
7.0	0.216	0.185	0.055	0.070	0.098

[a] Nominal thickness (casting bar settings).

Films made by method IV have a higher rate of dye uptake than those made by method I, the rate being almost independent of film thickness. The rate for a given film type and regeneration system increases with in-

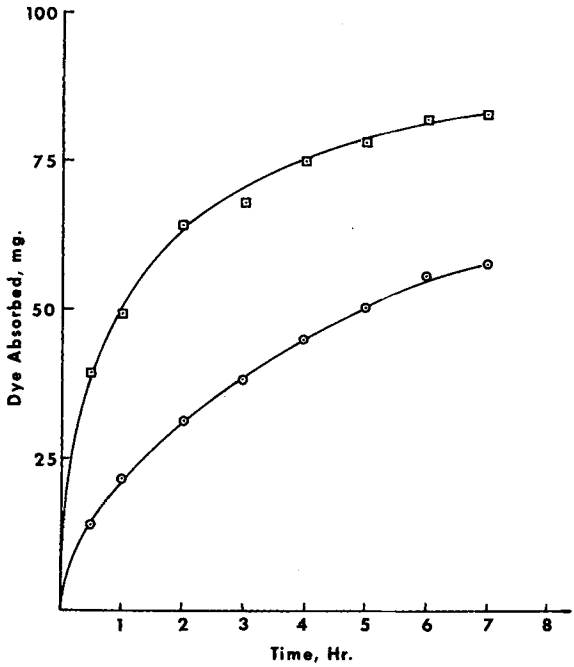

Fig. 1. Rate of dye absorption in films prepared by (⊙) method I and (⊡) method IV regeneration. Plotted are the quantities of dye absorbed by 36 in.^{2} of film from a 0.2% solution, containing a total of 100 mg.

creases in initial dye concentration, and in general, the dye uptake is always more rapid in the first few minutes than later.

In the preceding experiments, almost all of the dye was depleted from the solution in the course of an experiment. In order to have an estimate of the maximum dye capacity of these films at equilibrium, experiments were extended to 270 hr. In 100 ml. of 1.15% dye solution, the rate of dye

TABLE V
Amount of Dye Absorbed from 0.2% Dye Solution by Films Cast at 0.010 in. Bar Setting

	Amt. dye absorbed, mg./36 in.^{2}	
Time, hr.	Method I	Method IV
0	0	0
0.5	14.25	39.24
1.0	21.76	49.60
2.0	31.38	64.28
3.0	38.36	68.10
4.0	45.10	75.25
5.0	50.28	78.00
6.0	56.14	81.94
7.0	58.00	83.20

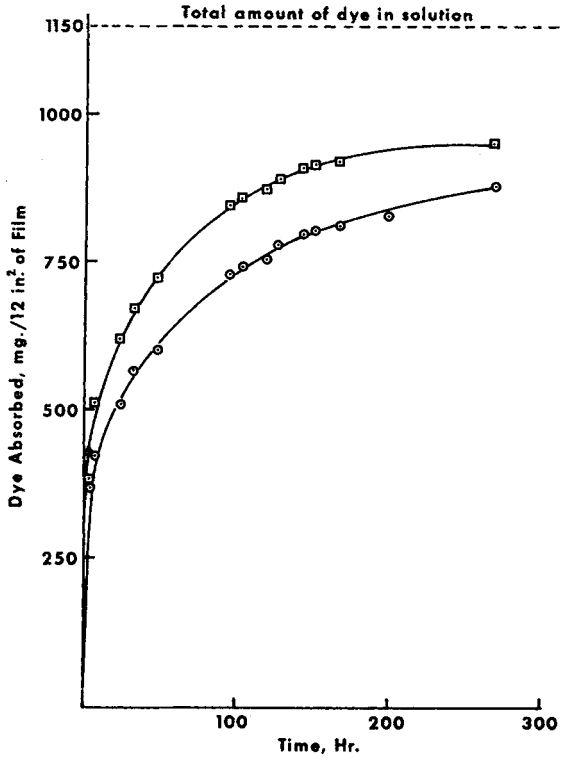

Fig. 2. Rate of dye absorption, to equilibrium, of films regenerated by (⊙) method I and (⊡) method IV.

TABLE VI
Maximum Amount of Dye Absorbed by Regenerated Film[a]

	Method I		Method IV	
Time, hr.	Optical density	Amt. absorbed, mg./36 in.²	Optical density	Amt. absorbed, mg./36 in.²
0	0.850	0	0.850	0
3	0.580	370	0.560	383
8	0.550	422	0.480	513
24	0.490	507	0.400	621
32	0.450	562	0.370	670
48	0.430	599	0.330	722
96	0.330	727	0.240	844
104	0.325	743	0.230	859
120	0.320	752	0.220	874
128	0.305	781	0.210	891
144	0.290	897	0.197	907
152	0.290	801	0.200	910
168	0.287	809	0.195	918
270	0.225	878	0.170	950

[a] Volume: 100 ml. of 1.15% dye solution (total amount of dye = 1150 mg.).

uptake for the two film types was measured on 3 × 4 in. films made at a bar setting of 0.010 in. The data are given in Table VI and displayed graphically in Figure 2.

This experiment reemphasizes that the rate as well as the total amount of dye uptake is greater in films regenerated by method IV than by method I. Under the conditions of experiment, method I films absorbed 76.3% of the total dye in solution, whereas method IV films absorbed 82.6%. On a weight basis this amounts to 2.67 and 3.09 mg. dye/mg. of cellulose, respectively.

Microscopy of Dyes Films

In an attempt to ascertain the location of the dye, several films were embedded in gum arabic and sectioned by microtome; the sections were

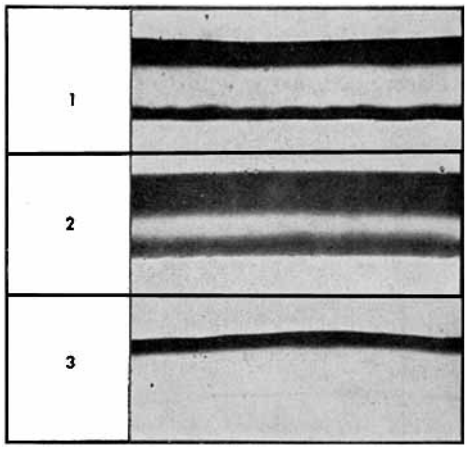

Fig. 3. Photomicrographs of dyed cross sections of cellulose films: (*1*) standard regenerating bath (I); (*2*) two-bath system (IV); (*3*) zinc sulfate added to bath (III).

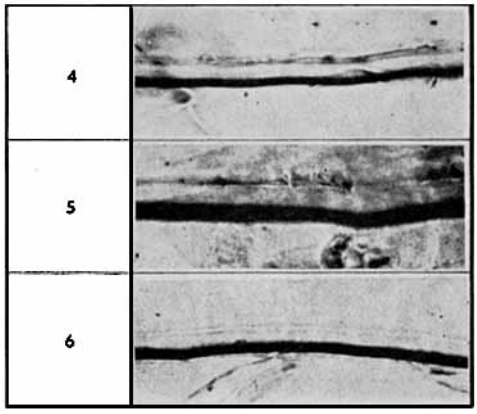

Fig. 4. Photomicrographs of cellulose films regenerated in a standard bath (method I) and redyed after washing: (*4*) 1 min. water wash, redyed; (*5*) 24-hr. water wash, redried; (*6*) 24-hr. water wash, redyed.

examined by phase-contrast microscopy. Photomicrographs were also made on 35-mm. Ektachrome film. (The microtoming technique is described below.)

Plate-cast viscose gel films were dyed in a 0.2% solution of dye for 5.0 min. and sectioned. Photographs taken at 100× magnification, followed by enlargement, are shown in Figure 3, including laboratory-cast films regenerated from a standard single bath (I), a two-bath system (IV), and a zinc sulfate-modified bath (III). The differences in dye penetration of these films confirm the dependency of cellulose fine structure on the regeneration process and on the chemical composition of regenerating solutions. The three photographs of Figure 4 confirm the diffusion process of dye penetration and its time dependency for standard viscose films prepared in the laboratory. They represent dyeing and washing experiments (No. 5, 8 hr.; No. 6, 21 hr. of washing) as described below.

Mechanism of Dye Transport

The experiments described above tend to show that in the initial stages of dyeing, rapid absorption occurs, followed by slow diffusion of the dye toward the interior.

To gain greater insight into the mechanism of dye transport, films were dyed, immersed in clear water, and then redyed. To this end, experiments as follows were performed to determine whether the dye distribution is

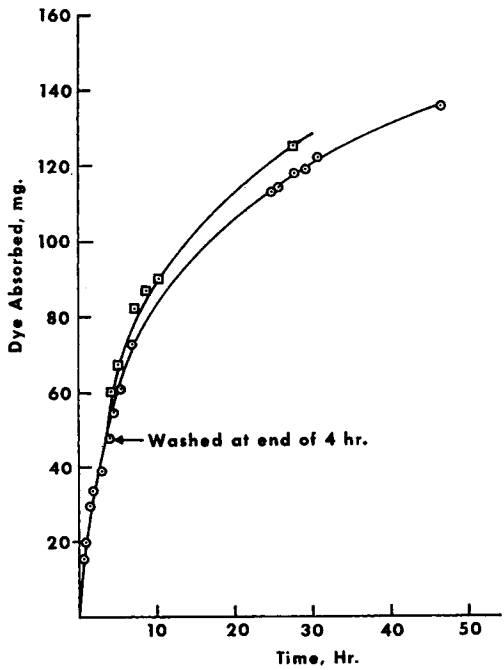

Fig. 5. Rate of dye absorption and effect of washing on dye uptake: (⊙) control; (⊡) after washing. The solution contained 211 mg. of dye.

TABLE VII
Optical Density of Films Washed in Water and Redyed

Time, hr.	Optical density			
	Control	Expt. 2[a]	Expt. 3[b]	Expt. 4[c]
0	0.390	0.390	0.392	0.385
0.5	0.365	0.370	0.370	0.365
1.0	0.360	0.365	0.365	0.360
1.5	0.345	0.350	0.350	0.347
2.0	0.340	0.345	0.347	0.340
3.0	0.335	0.330	0.330	0.330
4.0	0.320	0.315	0.315	0.317
4.5	0.310	0.305		
5.5	0.302	0.300		
7.0	0.280	0.280		
25.0	0.200	0.205	0.300[d]	0.305[d]
26.0	0.200	0.205	0.290	0.290
28.0	0.195	0.200	0.260	0.265
29.5	0.195	0.200	0.255	0.245
31.0	0.190	0.190	0.250	0.240
47.0	0.162	0.155	0.180	0.180

[a] At the end of 4 hr., the sample was immersed in water for 1 min. and replaced in the dye solution.

[b] At the end of 4 hr., the sample was removed, washed for 20.5 hr. in 100 ml. water, and replaced in the dye solution.

[c] Same treatment as expt. 3 in 200 ml. water.

[d] These samples had been replaced in the dye bath at 24.5 hr.

affected by immersion in water (plate-cast samples were regenerated by method I, and 3 × 4 in. specimens were dyed in 100 ml. of 0.2% aqueous dye solutions): (*1*) the rate was measured without washing (control); (*2*) a film dyed for 4 hr. was immersed in 100 ml. water for 1.0 min. (quick wash) and dyeing was resumed; (*3*) same as experiment (*2*) except that washing in water lasted 20.5 hr.; (*4*) same as experiment (*3*) except that 200 ml. water was used. Spectrophotometric values were obtained by diluting 1 ml. of dye solution to 100 ml. and measuring the optical density; the data obtained are presented in Table VII.

The amounts of dye lost in a 20-hr. leaching with water were 0.16 and 0.20 mg. (expts. 3 and 4, respectively). These values are very small as compared with 48 mg. of dye held by the film at the end of 4 hr. The amount of dye in the films was then calculated from the optical density measurements by use of the calibration curve and plotted as Figure 5.

A simple model to account for the facts of dye transport as observed in this system can be treated mathematically (Appendix) to give the expression,

$$-\ln(C/C_0) - (1 - C/C_0) = \alpha D t \gamma^2 C_0/C_f$$

where C is the dye concentration in the solution at time t, C_0 is the dye concentration in the solution initially, C_f is the concentration of dye in

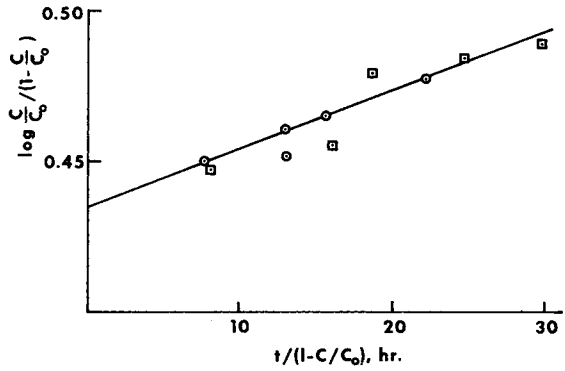

Fig. 6. Dye absorption as a function of time, log $(C/C_0)/(1-C/C_0)$ as a function of $t/(1-C/C_0)$, dye concentration 0.2%: (⊙) before washing; (⊡) after washing. The slope of the line is 0.40.

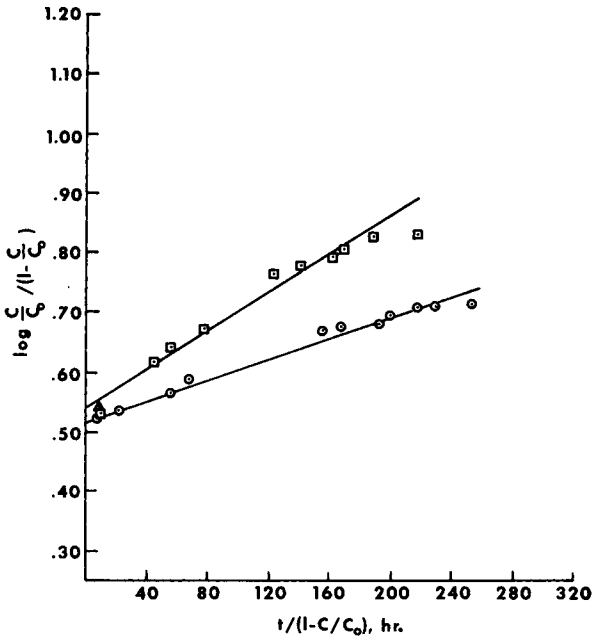

Fig. 7. Dye absorption as a function of time, log $(C/C_0)/(1-C/C_0)$ as a function of $t/(1-C/C_0)$, dye concentration 1.15%: (⊙) method I (slope 0.35); (⊡) method II (slope 0.64) regeneration.

the film at time, t, α is the partition coefficient of the dye between film and solution, D is the diffusion coefficient, and γ^2 is the ratio of film area to volume of the dye solution. If this diffusion equation is applied to the data in Table VII, a straight line (Fig. 6) results when log $(C/C_0)/(1 - C/C_0)$ is plotted as a function of $t/(1 - C/C_0)$. Similar results are obtained (Fig. 7) when the diffusion equation is applied to the data of Table VI (270

hr. of dyeing at a higher dye concentration). The travel of dye through the regenerated gel film is therefore mainly a diffusion process.

Interpretation of Results

Regenerated cellulose films have a tremendous capacity for absorbing Solophenyl Fast Blue Green BL. As much as 84% of the dye can be absorbed, based on the dry weight of cellulose. The rate of dye absorption and the amount of dye taken up by the film are, however, very sensitive to the structures of the film and the method which has been used to regenerate the cellulose.

The leaching experiments show the very great affinity of cellulose for this dye. They have indicated, further, that a quick wash with water does not affect the rate of dye uptake. Longer washing time, up to 20 hr., leads to an increase in the rate of dye uptake. Small but finite quantities of dye are removed in long washing, but the increased uptake exceeds the amount that could be accounted for by the dye loss. The ultimate capacity for taking up dye is not affected by washing, and the amount of dye extracted and the rate of subsequent dye uptake are independent of the volume of water used for washing.

In general, films made on a commercial casting machine have a much smaller tendency for dye absorption than do plate-cast films.

The two sides of a plate-cast film are different in nature, which is perhaps not surprising. The side that has been exposed to the regenerating bath is resistant to dye absorption, and the side which has been in contact with the glass plate has a high propensity for dye absorption. Modification of the regenerating bath alters this situation. Thus, use of zinc sulfate causes a decrease in the amount of dye taken up by films, while a system using a separate coagulating bath before regeneration results in dye pickup by both sides of the film and the dye uptake is about twice that obtained with a single bath system.

The diffusion behavior of the dye, the effect of prolonged water washes, and the microscopic examination of sections of dyed film all indicate that dye penetrates the film very slowly. Most of the dye is originally very close to the surface and then slowly migrates through the film. In these films there seems to be a barrier to dye penetration at or near the surface of one or both sides. This region might be a rather thin section, a cuticle of skinlike material. Film regenerated on a glass plate has one side, that which was away from the plate, through which dye cannot penetrate. If dyed for a sufficiently long time, dye will penetrate from the other side and will almost reach this surface.

Our experiments indicate that, save for a thin surface layer, the fine structure of cellophane films is similar to the core structure of rayon fibers having a relatively high degree of lateral order. This core structure is covered by a very thin skin whose crystalline order and thickness is a function of the type of regeneration used and the regenerating solution employed. Our experiments seem to indicate that the principal differences

among films result from the existence of these barriers rather than from differences in the rate of diffusion through the main body of cellulose. If this be true, the surface barrier will affect the accessibility of the film, not only to dye but also to moisture and softener, and may be the controlling factor in softener uptake of films for softeners of large molecular volume.

APPENDIX

Derivation of a Mathematical Model for Dye Diffusion

In constructing a simple mathematical model for the process of dye diffusion through cellulose films, it may be assumed that the diffusion constant for the dye in the film is independent of the local dye concentration. Provided the dye concentration is sufficiently high and the sample size sufficiently small, a time can be conveniently chosen during which there is little change in the concentration of the dye solution. As we have shown from photomicrographs of sections of dyed film, there is little or no dye at the center of the film in the time considered. Under these conditions the film may be considered a semi-infinite solid for which the distribution of dye is given by the expression,

$$C_f = \alpha C_s\{1 - \text{erf}[x/(2Dt)^{1/2}]\}$$

wherein C_f is the dye concentration in the film at a distance x centimeters from the surface at a time t seconds after immersion of the film in the dye solution, C_s the concentration of the dye solution, D the diffusion constant; erf is the error function, and α is a proportionality constant for the partition of dye between film and solution.

The rate at which dye penetrates the film surface (i.e., is removed from the dye solution) is given by the expression

$$dN/dt = -DA(\partial C/\partial x)_{x=0} \tag{1}$$

where N is the amount of dye removed from solution.

Since

$$C_f = \alpha C_s[1 - \text{erf}(x/2Dt)^{1/2}]$$

and

$$\partial C/\partial x = [\alpha C_s(-2/\pi^{1/2})(1/Dt)^{1/2} \exp\{-x^2/2Dt\}]/2$$

$$dN/dt = \alpha C_s A(D/\pi t)^{1/2} \tag{2}$$

On integrating eq. (2),

$$N = \int_0^t (dN/dt)dt = 2\alpha C_s A(Dt/\pi)^{1/2} \tag{3}$$

and the concentration in the solution at time t is

$$C_s = C_s^\circ - 2\alpha C_s^\circ A(Dt/\pi)^{1/2}/V_s \tag{4}$$

wherein V_s is the volume of solution and A is the surface area of the film.

In this derivation we have assumed that the change in solution concentration is sufficiently small that it does not affect the rate of uptake of dye from solution.

An alternative derivation allows us to take care of this possibility. In this derivation we assume: (*1*) that the concentration in the film has a constant value C_f and fills a layer of thickness y; (*2*) that the rate of transport of dye across this layer is proportional to the dye concentration in solution and inversely proportional to the thickness y.

The rate of dye transport is then given by the expression,

$$dN/dt = \alpha DAC_s/y \tag{5}$$

The total amount of dye in the film is given by $N = C_f yA$, from which it follows that

$$dN/dt = (\alpha C_s C_f)^{1/2}(D/2t)^{1/2}A \tag{6}$$

Equation (6) is of the same form as eq. (2), and hence may be used in its place, since both make similar predictions about the rate of uptake of dye from solution. Equation (6) can be easily modified to allow for the depletion of dye from solution, by noting that from the above assumptions,

$$N = C_f yA = (C_s^\circ - C_s)V_s \tag{7}$$

Then eq. (5) becomes

$$-dN/dt = -V_s dC_s/dt = \alpha DA^2 C_s C_f/(C_s^\circ - C_s)V_s \tag{8}$$

On integrating eq. (8), we obtain

$$-\ln(C/C_0) - (1 - C/C_0) = \alpha Dt\gamma^2 C_0/C_f \tag{9}$$

wherein C is the dye concentration in solution at time t, C_0 is the initial dye concentration in solution, C_f is the dye concentration in the film, γ^2 is the ratio of film area to volume of dye solution, and D is the diffusion coefficient.

Sectioning and Mounting of Cellophane Samples for Photomicrography*

The procedure involves embedding a small strip of film between two layers of gum arabic, which are allowed to harden. The excess gum is removed to form a sticklike piece of embedded film, and this is then mounted in paraffin on a fiber block. A microtome is used to cut cross sections of the mounted film which are transferred to microscope slides and mounted in Permount (Fisher Scientific Co.) under glass cover slips.

The embedding gum is prepared from 44 ml. water, 6 ml. 2B denatured ethyl alcohol, 10 ml. glycerol, and 50 g. gum arabic. After the ingredients have been combined, a white scum forms, and this should be removed. The mixture is then heated on a boiling water bath for $^1/_2$ hr. and allowed to cool. Reheating may be necessary, until the gum finally becomes dark

* The brief description given here is essentially a procedure given us by Mr. P. E. Latreille, International Cellulose Research Limited, Hawkesbury, Ontario.

brown, clear, and of the consistency of honey (it may be stored indefinitely if kept well sealed away from air).

To prepare a sheet of gum for the bottom part of the embedding medium, a microscope slide is thinly smeared with vaseline or a silicone, and a small amount of gum is placed on the coated slide and allowed to dry for about 24 hr. With a razor blade, the edges are cut away to form a rectangle about $1^1/_2 \times {}^1/_2$ in. Then a small strip of the cellophane to be sectioned is cut (about ${}^1/_4 \times {}^3/_4$ in.) and placed in the center of the rectangular piece of gum. More liquid gum is spread over the cellophane sample and allowed to dry. (After several hours, the excess gum should be removed from around the cellophane with a razor blade so that the gum will dry faster close to the film.) Enough excess gum should be cut away to leave a narrow margin of gum along each long edge of the film, so that a sticklike mold of embedded gum results.

When the gum in which the film has been embedded has dried but is still flexible, it is mounted in paraffin on a wooden or fiber block. Fiber blocks about ${}^1/_2 \times {}^3/_4 \times {}^3/_4$ in., with three parallel grooves cut along the top surface, were used. Peel-A-Way embedding molds for the paraffin were obtained from Lipshaw Mfg. Co., Detroit.

The stick of embedded film is inserted on end into the center groove of a fiber block (if the gum is too thick, it may be tapered with a razor blade to make it fit). The paraffin is melted over low heat and poured into one of the Peel-A-Way molds (if the paraffin is too hot, it may melt the mold). The fiber block with the embedded film secured to it is then inverted and held with the film pointing downward in the liquid paraffin. About 5 min. is required for the paraffin to harden. While the paraffin is hardening, care must be taken to keep the film sample vertical and straight with respect to the block; if it is more than about ${}^3/_4$ in. long, it may buckle against the bottom of the Peel-A-Way mold. When the paraffin has completely cooled, the mold is peeled away, and the excess paraffin is then pared off with a fresh razor blade and tapered slightly at the end.

A rotary microtome was used to cut sections at a thickness of 17 μ. It seemed preferable to position the specimen so that the length direction of the cross section of the piece of film was horizontal rather than vertical.

The transferral of the microtomed sections from the knife to a microscope slide is a delicate operation (a small sewing needle serves the purpose well). Once a cross section has been placed on a slide, the gum may be quite strongly secured to the glass by pressing with a needle and flattening the specimen somewhat. This helps insure that the cross-section of film will lie flat on the slide, and not on edge. The surrounding paraffin can usually be removed with the needle. The sections are then covered with a drop or two of toluene to dissolve any remaining paraffin, and viewed in a phase-contrast microscope at a magnification of 100× or greater.

Four or five sections of film can be placed sufficiently close together on a slide to be covered with a single cover slip. When the sections are ready to be mounted, one or two drops of Permount histological mounting medium

are placed so that they cover the film sections (Permount is soluble in toluene; it should be added while a small amount of toluene still covers the sections). The cover slip is then placed on the sections, care being taken to avoid trapping air bubbles between the cover slip and the slide. The finished slides are then set next to a hot plate, so that they are at about 50°C., with slight pressure on the cover slips until the Permount has dried.

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Résumé

Nous avons démontré l'utilité des techniques de coloration au moyen du bleu vert BL solophényl capide pour caractériser une variété de films cellulosiques regénérés. La mesure du rapport de densité optique, de la vitesse et de l'intensité de fixation de colorant montrent que des différences de structures existent dans les films de cellulose regénérée réalisés dans deux différentes conditions. Ces différences sont attribuées aux différences dans l'ordre latéral et dans l'orientation des chaînes de la cellulose et sont considérées comme identiques aux films et aux squelettes observés dans les fibres de rayonne. On a trouvé que ces différences se rattachent d'une façon reproductible aux différences dans les conditions de régénération et de transformation. La diffusion du colorant à travers un film est très rapide au début, et relentit ensuite jusqu'à une vitesse presque constante; dépendant de la concentration en colorant dans la solution et du type de film. Une équation de diffusion modifiée de la forme $\ln C/C_0 - (1 - C/C_0) = D\gamma^2 tC_0/C_f$ a été trouvée adéquate pour exprimer l'état non-stationnaire du procédé d'absorption observé, où C_0 est la concentration initiale en colorant de la solution type, C la concentration instantanée de colorant au temps t, C_f la concentration en colorant dans le film, γ^2 la surface du film par unité de volume de solution de colorant, et D le coefficient de diffusion. Ainsi, on apporte une base mathématique pour la différentiation structurale dans des films cellulosiques réalisés de diverses manières. Les films de viscose coulés en plaques, semblent avoir une surface dense (film) exposée au bain de régénération et une surface poreuse (squelette) sur le côté touchant la plaque, tandis que les films de viscose coulés à la machine ont une surface dense sur les deux côtés.

Zusammenfassung

Die Brauchbarkeit von Anfärbeverfahren mit Solophenyl Fast Blue Green BL zur Charakterisierung einer Vielzahl regenerierter Zellulosefilme wurde gezeigt. Messung des optischen Dichteverhältnisses sowie der Geschwindigkeit und des Umfangs der Farbstoffaufnahme zeigt, dass in den unter uerschiedenen Bedingungen hergestellten Zellulosefilmen Strukturnterschiede bestehen. Diese Unterschiede werden auf Unterschiede in der seitlichen Ordnung und Orientierung der Zelluloseketten zurückgeführt und scheinen den bei Rayonfasern beobachteten Unterschieden bei der sogenannten Haut und dem sogenannten Kern ähnlich zu sein. Diese Unterschiede lassen sich-

reproduzierbar zu Unterschieden der Regenerierungsund Prozebbedingungen in Beziehung setzen. Farbstoffdiffusion in einen Film ist anfangs sehr rasch und verlangsamt sich später zu einem fast konstanten Wert, der von der Farbstoffkonzentration in der Lösung und vom Filmtyp abhängt. Mit einer modifizierten Diffusionsgleichung von der Form $\ln C/C_0 - (1 - C/C_0) = D\gamma^2 tC_0/C_f$, wo C_0 die Anfangsfarbkonzentration der Testlösung, C die momentane Farbstoffkonzentration zur Zeit t, C_f die Farbstoffkonzentration im Film, γ^2 die Filmoberfläche pro Volumseinheit der Farbstofflösung und D der Diffusionskoeffizient ist, kann den nicht stationären Zustand des beobachteten Absorptionsprozesses befriedigend wiedergeben. Sie liefert so eine mathematische Grundlage für die strukturelle Differentiierung von Zellulosefilmen, die nach verschiedenen Verfahren erhalten wurden. Plattengegossene Viskosefilme scheinen gegen das Regenerierungsbad eine dichte Oberfläche (Haut) und an der die Platte berührende Seite eine poröse Oberfläche (Kern) zu besitzen, während maschinengegossene Viskosefilme an beiden Seiten eine dichte Oberfläche haben.

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